

Nonergodicity parameters for a molecular liquid: A comparison between mode coupling theory and simulation

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We apply the mode coupling theory (MCT) which was recently worked out for molecular liquids to a liquid of diatomic, rigid molecules. Making use of the static correlators $S_{ll'}^m(q)$ from a molecular dynamical simulation, we have solved the MCT-equations for the nonergodicity parameters $f_l^m(q) = \lim_{t \rightarrow \infty} S_{ll}^m(q, t)/S_{ll}^m(q)$, assuming that all correlators are nonzero for $l = l' = 0, 1, \dots, l_{co}$, only. Depending on $l_{co} = 0, 1, 2$ we obtain different types of ideal glass transitions with transition temperatures $T_c^{(l)}$ which are below T_c^{MD} as deduced from the MD-simulation. The q -dependence of the critical nonergodicity parameter $(f_l^m)_c^{MD}$ from the simulation is reasonably well reproduced by the corresponding MCT-result. The influence of a strong and weak diagonalization approximation on the results is discussed.

I. INTRODUCTION

The use of mode coupling theory (MCT) is one of the most important attempts to describe the *structural* glass transition. Restricted to *simple* liquids, it has provided an equation of motion for the normalized density correlator

$$\Phi(q, t) = \frac{S(q, t)}{S(q)} \quad (1)$$

where $S(q)$ is the corresponding static correlation function. MCT, in its *idealized* version, interprets the glass transition as a dynamical transition at a critical temperature T_c (or critical density n_c) from an ergodic (supercooled liquid) to a nonergodic phase (glass). In the latter phase the density $\rho(q, t)$ does not approach its equilibrium value $\rho_0 = \langle \rho(q, t) \rangle$ in the long time limit, i.e. the correlation function $\Phi(q, t)$ of the density fluctuations $\delta\rho(q, t) = \rho(q, t) - \rho_0$ does not decay to zero for $t \rightarrow \infty$. Therefor one can use the nonergodicity parameter (NEP)

$$f(q) = \lim_{t \rightarrow \infty} \Phi(q, t) \quad (2)$$

as an order parameter for the glass transition. $f(q)$ vanishes above and becomes nonzero at T_c . In the long time limit $t \gg t_0$ the MCT-equations involve only $S(q)$ as an input quantity. Here, t_0 is a microscopic time of order 10^{-13} sec. This fact demonstrates the *microscopic* nature of MCT, because $S(q)$ can be calculated from the potential energy $V(\mathbf{x}_1, \dots, \mathbf{x}_N)$ which only depends on the microscopic configuration $\{\mathbf{x}_n\}$ of the particles. The discussion of the MCT-equations for T in the vicinity of T_c leads to several interesting predictions for the time and temperature dependence of $\Phi(q, t)$. However, due to the existence of ergodicity restoring processes in real glass formers below T_c , which are taken into account by the *extended* MCT, the transition is smeared out. Nevertheless, a couple of experimental and numerical investi-

gations have clearly shown the validity of several predictions of idealized MCT. For more details the reader may consult the reviews [1–6].

These tests of idealized MCT (simple liquids) were mainly *qualitative*, i.e. the validity of the asymptotic power laws for the α - and β -relaxation regimes was studied. Only very few *quantitative* test exist, which is, besides the calculation of the critical temperature (or critical density), the q -dependence of the critical NEP $f^c(q)$ at T_c (or n_c) and the critical amplitude $h(q)$. This was done for a monoatomic [7] (only T_c was determined) and binary Lennard-Jones liquid [8], for a hard sphere [9] and a soft sphere system [2,10] and for the molecular liquids orthoterphenyl [11] and water [12]. Although the two latter liquids contain orientational degrees of freedom (ODOF), the analysis of the experimental [11] and numerical results [12] was done in the framework of MCT for *simple* liquids, which does not account for the ODOF. A first attempt to include ODOF and their coupling to the translational degrees of freedom (TDOF) has recently been made for water [13]. These authors suggest a semi-schematic model where the full q -dependence is considered, but the influence of the ODOF is condensed in a single parameter χ_R . The phenomenological introduction of χ_R can be viewed as a “renormalisation” of the mode coupling strength for the TDOF (center of mass).

Because most of the glass formers are of molecular origin, it is important to extend MCT to *molecular* liquids. This has recently been done for a single dumb-bell molecule in an isotropic liquid [14], for linear molecules [15] and arbitrary molecules [16–18]. In the present paper we will perform a quantitative test of the molecular MCT for a liquid of rigid diatomic molecules by comparing the corresponding nonergodicity parameters as obtained from a recent MD-simulation with those from molecular MCT.

The outline of our paper is as follows. The next section contains a description of the molecular MCT-equations

for linear molecules. The diatomic liquid and the computational details are described in section 3. Section 4 contains the comparison between MCT and numerical results and the final section presents a summary and some conclusions.

II. MOLECULAR MCT

In this section we give a short summary of the application of MCT to molecular liquids. We will restrict ourselves to linear molecules. For details the reader is referred to Ref. [15]. The starting point is the tensorial one-particle density

$$\rho_{lm}(\mathbf{q}, t) = \sqrt{4\pi} i^l \sum_{n=1}^N \exp(i\mathbf{q} \cdot \mathbf{x}_n(t)) Y_{lm}(\Omega_n(t)),$$

$$l = 0, 1, 2, \dots, -l \leq m \leq l \quad (3)$$

where $\mathbf{x}_n(t)$ and $\Omega_n(t) = (\theta_n(t), \phi_n(t))$ are, respectively, the center of mass position and the Euler angles of the n -th molecule at time t . Due to the axial symmetry of the molecule the third Euler angle $\chi_n(t)$ does not play a role. N is the number of molecules and Y_{lm} are the spherical harmonics. The factor in front of the sum is for technical convenience. The generalization of the density correlator $S(q, t)$ (cf. eq.(1)) to molecular liquids of linear molecules is straightforward:

$$S_{lm, l'm'}(\mathbf{q}, t) = \langle \rho_{lm}^*(\mathbf{q}, t) \rho_{l'm'}(\mathbf{q}, 0) \rangle \quad (4)$$

where $*$ denotes complex conjugation and the angular brackets refer to the canonical average over the initial conditions in phase space. Generally, the correlation matrix $\mathbf{S}(\mathbf{q}, t) \equiv (S_{lm, l'm'}(\mathbf{q}, t))$ is nondiagonal in both l and m . In the q -frame, i.e. for $\mathbf{q} = \mathbf{q}_0 \equiv (0, 0, q)$, $q = |\mathbf{q}|$, $\mathbf{S}(\mathbf{q}, t)$ becomes diagonal in m :

$$S_{lm, l'm'}(\mathbf{q}_0, t) \equiv S_{ll'}^m(q, t) \delta_{mm'} \quad (5)$$

The matrix elements $S_{ll'}^m(q, t)$ are real, and nonzero for $0 \leq |m| \leq \min(l, l')$, only. In addition they fulfill [15]

$$S_{ll'}^{-m}(q, t) = S_{ll'}^m(q, t). \quad (6)$$

In the third and fourth section we will restrict ourselves to those correlators with $l = l' = 0, 1$ and 2. In that case, only six independent correlators $S_l^m(q, t) \equiv S_{ll}^m(q, t)$, $0 \leq m \leq l$ exist.

A closed set of equations can be derived for the Laplace transform $\hat{\mathbf{S}}(\mathbf{q}, z)$ of $\mathbf{S}(\mathbf{q}, t)$ by use of the Zwanzig-Mori projection formalism in combination with the mode coupling approximation which replaces the slow part of the time dependent memory kernel by a linear combination of bilinear terms $S_{l_1 m_1, l'_1 m'_1}(\mathbf{q}_1, t) S_{l_2 m_2, l'_2 m'_2}(\mathbf{q}_2, t)$. The final result for the MCT-equations is as follows [15]:

$$\hat{\mathbf{S}}(\mathbf{q}, z) = - \left[z \mathbf{1} + \hat{\mathbf{K}}(\mathbf{q}, z) \mathbf{S}^{-1}(\mathbf{q}) \right]^{-1} \mathbf{S}(\mathbf{q}) \quad (7)$$

with

$$\hat{K}_{lm, l'm'}(\mathbf{q}, z) = \sum_{\alpha\alpha'} q_l^\alpha(\mathbf{q}) q_{l'}^{\alpha'}(\mathbf{q}) \hat{k}_{lm, l'm'}^{\alpha\alpha'}(\mathbf{q}, z) \quad (8)$$

$$q_l^\alpha(\mathbf{q}) = \begin{cases} q & , \quad \alpha = T \\ \sqrt{l(l+1)} & , \quad \alpha = R \end{cases} \quad (9)$$

and

$$\hat{k}(\mathbf{q}, z) = - \left[z \mathbf{J}^{-1} + \mathbf{J}^{-1} \hat{\mathbf{M}}(\mathbf{q}, z) \mathbf{J}^{-1} \right]^{-1}. \quad (10)$$

$\mathbf{J} \equiv (J_{lm, l'm'}^{\alpha\alpha'})$ is the correlation matrix of the translational ($\alpha = T$) and rotational ($\alpha = R$) current density $j_{lm}^\alpha(\mathbf{q})$ [15]. The kernel $\mathbf{J}^{-1} \mathbf{M}(\mathbf{q}, t) \mathbf{J}^{-1}$ cannot be calculated exactly. The mode coupling approximation yields for its slow part (which determines the long time relaxation):

$$\begin{aligned} \left[(\mathbf{J}^{-1} \mathbf{M}(\mathbf{q}, t) \mathbf{J}^{-1})_{\lambda\lambda'}^{\alpha\alpha'} \right]_{\text{slow}} &\approx m_{\lambda\lambda'}^{\alpha\alpha'}(\mathbf{q}, t) = \\ &= \frac{1}{2N} \sum_{\mathbf{q}_1 \mathbf{q}_2} \sum_{\lambda_1 \lambda_2 \lambda'_1 \lambda'_2} V^{\alpha\alpha'}(\mathbf{q} \lambda \lambda' | \mathbf{q}_1 \lambda_1 \lambda'_1; \mathbf{q}_2 \lambda_2 \lambda'_2) \times \\ &\times S_{\lambda_1 \lambda'_1}(\mathbf{q}_1, t) S_{\lambda_2 \lambda'_2}(\mathbf{q}_2, t). \end{aligned} \quad (11)$$

Here we have used the short hand notation $\lambda = (l, m)$. The vertices $V^{\alpha\alpha'}$ only depend on the static correlators $S_{\lambda\lambda'}(\mathbf{q})$ or equivalently on the direct correlations functions $c_{\lambda\lambda'}(\mathbf{q})$. The explicit expression for $V^{\alpha\alpha'}$ can be found in Ref. [15]. Eqs.(7)–(11) are the closed set of MCT-equations for linear molecules, and their structure is quite similar to that of the MCT-equations for simple liquids. But due to the presence of ODOF and their coupling to TDOF, which is in the vertex functions $V^{\alpha\alpha'}$, the mode coupling polynomial (11) is much more involved. Therefore, in a first step we will simplify these equations by assuming diagonality of $\mathbf{S}(\mathbf{q}, t)$ and $\mathbf{m}(\mathbf{q}, t)$ with respect to l . We stress that this diagonalization approximation is also assumed for the static correlators, in order to keep the coupled set of equations as simple as possible. Since \mathbf{J} is already diagonal, eqs.(7)–(11) allow for a self consistent solution for the normalized correlators

$$\Phi_l^m(q, t) = \frac{S_{ll}^m(q, t)}{S_{ll}^m(q)} \quad (12)$$

in the q -frame. Then, the corresponding nonergodicity parameters

$$f_l^m(q) = \lim_{t \rightarrow \infty} \Phi_l^m(q, t) = - \lim_{z \rightarrow 0} z \hat{\Phi}_l^m(q, z) \quad (13)$$

are solutions of the following set of coupled equations:

$$f_l^m(q) = \left[1 + \sum_{\alpha\alpha'} q_l^\alpha(q) q_{l'}^{\alpha'}(q) \left([F_l^m(q; \{f_l^m(q)\})]^{-1} \right)^{\alpha\alpha'} \right]^{-1} \quad (14)$$

with the 2x2 matrix

$$F_l^m = \begin{pmatrix} (F_l^m)^{TT} & (F_l^m)^{TR} \\ (F_l^m)^{RT} & (F_l^m)^{RR} \end{pmatrix}. \quad (15)$$

In the thermodynamic limit it is:

$$\begin{aligned} (F_l^m(q; \{f_l^m(q)\}))^{\alpha\alpha'} &= \\ &= \int_0^\infty dq_1 \int_{|q-q_1|}^{q+q_1} dq_2 (H_l^m(q, q_1, q_2; \{f_l^m(q)\}))^{\alpha\alpha'} \end{aligned} \quad (16)$$

where

$$\begin{aligned} (H_l^m(q, q_1, q_2; \{f_l^m(q)\}))^{\alpha\alpha'} &= \\ &= \sum'_{l_1 l_2} \sum_{m_1 m_2} v^{\alpha\alpha'}(qlm|q_1 l_1 m_1; q_2 l_2 m_2) f_{l_1}^{m_1}(q_1) f_{l_2}^{m_2}(q_2). \end{aligned} \quad (17)$$

$\sum'_{l_1 l_2}$ denotes the summation over l_1 and l_2 such that

$$\begin{aligned} l_1 + l_2 + l &\text{ is even} \\ |l_1 - l_2| &\leq l \leq l_1 + l_2. \end{aligned} \quad (18)$$

This restriction results from the Clebsch–Gordon coefficients $C(l_1 l_2 l; 000)$ which enter into $v^{\alpha\alpha'}$. The expressions for the $v^{\alpha\alpha'}$ are rather involved. Therefore we do not give them explicitly, here. They can be deduced from $V^{\alpha\alpha'}$ (see second paper of ref. [15]) by use of:

- i) transformation to the q-frame where one has to use the transformation properties of the correlators under rotations (see again second paper of ref. [15])
- ii) the diagonalization approximation with respect to l and
- iii) the thermodynamic limit $N \rightarrow \infty, V \rightarrow \infty$ such that $N/V = \text{const}$, which replaces the sums over $\mathbf{q}_1, \mathbf{q}_2$ in eq.(11) by integrals; then taking into account the conservation of momentum $\mathbf{q} = \mathbf{q}_1 + \mathbf{q}_2$ and performing the angular integration one obtains the integral representation of eq.(16)

$V^{\alpha\alpha'}$. This type of approximation will be called *weak* diagonalization approximation (WDA). Assuming in addition the diagonality of $v^{\alpha\alpha'}$ with respect to α , and accordingly the diagonality of F_l^m (which we call the *strong* diagonalization approximation (SDA)), the eqs.(14)–(17) simplify even more. It is the SDA which has been used for the calculation of $f_l^m(q)$ for a dumb-bell molecule in a liquid of hard spheres [14] and for a system of dipolar hard spheres [15]. The diagonalization approximation for the time-dependent *and* the static correlators with respect to the l 's implies (18). This restriction has two consequences. First, the eq.(14) for the f_l^m with l even may contain on its r.h.s. bilinear terms $f_l^m f_l^m$, but for l odd this cannot happen. Therefore f_l^m with l even

will exhibit a type-B transition and those with odd l may show a type-A or type-B transition. In case of a type-A transition the corresponding transition temperature is below that of the type-B transition for f_l^m with l even. Second, whereas eq.(14) for f_0^0 contains on its r.h.s. $f_0^0 f_0^0, f_1^{m_1} f_1^{m_2}, f_2^{m_1} f_2^{m_2}$ etc., the equation for, e.g. f_2^m involves $f_1^{m_1} f_1^{m_2}, f_2^{m_1} f_2^{m_2}, f_0^0 f_2^{m_2}$ etc., but *not* $f_0^0 f_0^0$, due to the diagonalization approximation of the *static* correlators. Therefore the freezing of the center of mass order parameter f_0^0 does not necessarily imply the freezing of f_2^m . f_2^m may freeze at a lower temperature via a type-B transition. Without the diagonalization approximation with respect to the l 's, we expect *all* $f_l^m(q)$ to freeze via a type-B transition at a *single* critical temperature T_c . For more details on type-A and type-B transitions the reader is referred to the schematic models which are discussed in ref. [1] and in ref. [19].

III. MODEL

In order to test the MCT-predictions, a MD-simulation for a system of diatomic, rigid molecules [20–22] was performed. Each molecule is composed of two different Lennard–Jones particles A and B, which are separated by a distance d . Both particles have the same mass m . The interaction between two molecules is given by the sum of the interactions between the four particles which are given by the Lennard–Jones potentials $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} [(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$. The Lennard–Jones parameters are given by $\sigma_{AA} = \sigma_{AB} = 1$, $\sigma_{BB} = 0.95$, $\epsilon_{AA} = \epsilon_{AB} = 1$ and $\epsilon_{BB} = 0.8$. We use lengths in units of σ_{AA} and ϵ_{AA} is taken as unit for the temperature ($k_B = 1$). In these units we have found that $d = 0.5$ is an appropriate value in order to avoid formation of a liquid crystalline phase. The MD-simulation was done for $N = 500$ molecules in an (N,p,T)-ensemble with $p = 1.0$ and T between 0.477 and 5.0 by use of the rattle algorithm. The length of the runs was long enough in order to prepare a well equilibrated system. In order to increase the statistics, average over at least eight independent runs was performed. One of the main results we have found is the existence of a type-B transition with a *single* transition temperature $T_c^{MD} \cong 0.475$, at which the dynamics crosses over from ergodic to quasi-nonergodic behavior. This temperature has been deduced from the α -relaxation time of the purely orientational (i.e. $q = 0$ in eq. 4) [20], purely translational (i.e. $l = l' = 0$ in eq.(4)) [21] and of the general correlators where $q \neq 0$ and $l = l' \neq 0$ [22]. The critical temperature T_c can be located within about 2% from these data. For more details the reader is referred to refs. [20–22].

IV. RESULTS

As already mentioned in section II we need for the solution of eqs.(14)–(17) the static correlators $S_{ll'}^m(q)$ as a function of (q, l, l', m) and temperature T . We remind the reader that we use the q -frame representation, without restricting generality. The MD-result for $S_{ll'}^m(q)$ is shown in Figure 1 for $T = 0.49$ and for $l = l' = 0, 1, 2$. The vari-

ation of $S_l^m(q) \equiv S_{ll}^m(q)$ with temperature is smooth. From this Figure we observe that the q -dependence of $S_l^m(q)$ strongly depends on l and m . Whereas $S_0^0(q)$ and $S_1^0(q)$ resembles the behavior of $S(q)$ for a simple liquid, with e.g. a well pronounced main maximum at $q_{max} \approx 2\pi$, the q -dependence of the other correlators is qualitatively different. For instance S_2^1 has its main peak at $q = 0$.

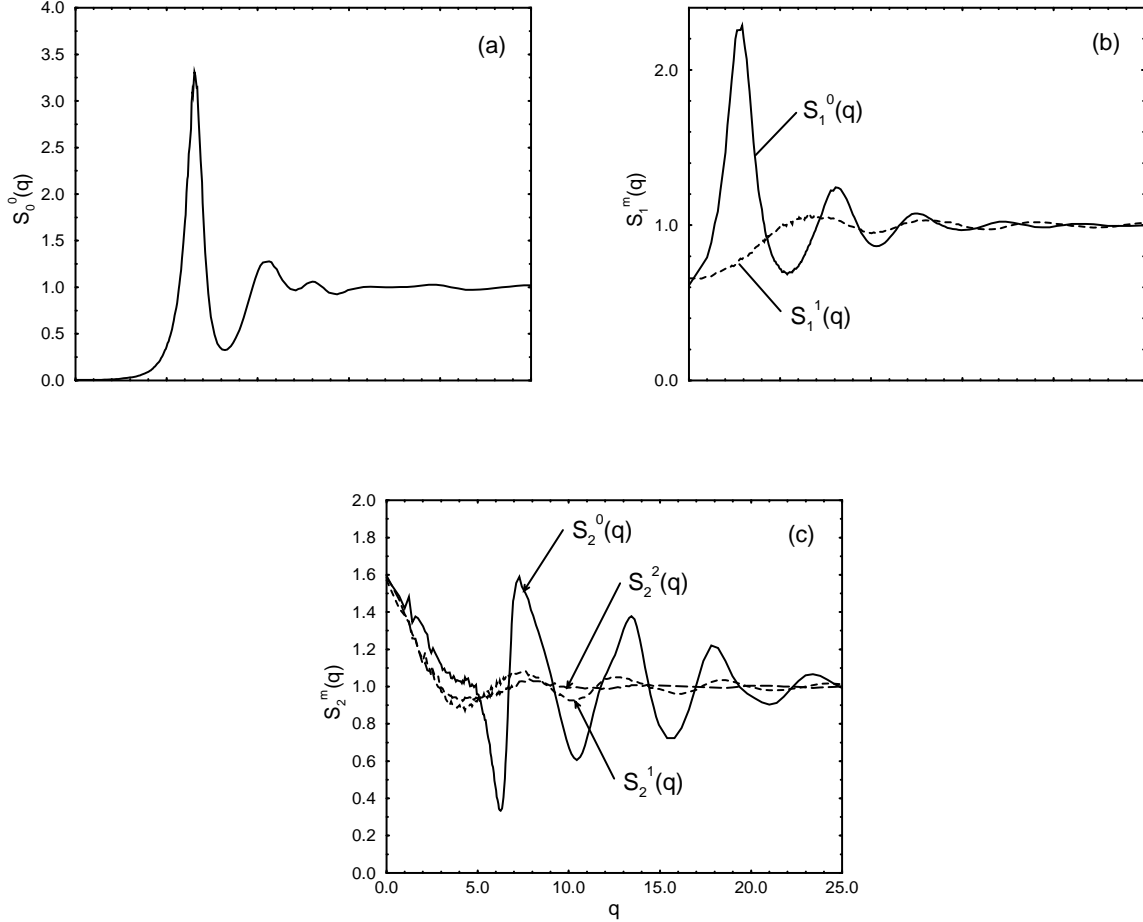


FIG. 1. $S_l^m(q)$ versus q for $T = 0.49$: (a) $l = m = 0$, (b) $l = 1, m = 0, 1$ and (c) $l = 2, m = 0, 1, 2$.

As will be seen below, we need $S_l^m(q)$ for temperatures below $T_{min} = 0.477$, the lowest value of our MD-simulation. This has been achieved by a linear extrapolation from the higher temperature regime ($T \geq 0.477$). After smoothing the q -dependence of $S_l^m(q)$ by a spline under tension, equations (14)–(17) were solved by iteration. This procedure is standard and had been used for simple liquids (see e.g. [1] and [8]). The iteration was stopped after the maximum value of $|(f_l^m(q))^{(\nu+1)} - (f_l^m(q))^{(\nu)}|$ was less than 10^{-6} . We have used SDA and WDA (see section II). The l -dependence has been truncated at $l_{co} = 0, 1$ and 2. The integrations

in (16) were performed numerically. For this the interval $[0, q_{co}]$ was divided into 300 *equidistant* grid points. Since the MD-data were limited to $q \leq q_{co} = 25$, we were not able to check the sensitivity of the results for $f_l^m(q)$ on a variation with q_{co} . But there should not be a considerable change by extending q_{co} to higher values than 25, because $S_l^m(q)$ already approaches one for $q = 25$ (for S_{22}^0 this is not quite true) (cf. Fig.1).

Special attention must be paid to $q = 0$. Since $(F_l^m(q, \{f_l^m(q)\}))^{\alpha\alpha'}$ for $l \neq 0$ is proportional to q^{-2} and q^{-1} for $\alpha = \alpha' = T$ and $\alpha \neq \alpha'$, respectively, we have treated eq. (14) separately for $q = 0$ and

$q \geq q_{min} \cong 0.08$. The results for $f_l^m(q)$ in between were obtained by a polynomial interpolation of degree four.

The first observation we make is that $f_l^m(q) \equiv 0$ for $T \geq 0.477$. This result, which holds for SDA, WDA and $l_{co} = 0, 1, 2$, is unexpected, because for all known cases MCT overestimates the transition temperature T_c . For instance, it is $T_c^{MCT} \approx 2T_c^{MD}$ for the binary Lennard-Jones liquid [8]. For $T < T_c^{MD} \cong 0.475$ ideal glass transitions are found for our molecular liquid. The transition temperatures are given in Table 1. Here a comment is in order. The transition temperatures are determined within an accuracy of 10^{-3} . Since the critical NEP vary as $(T - T_c)^{\frac{1}{2}}$ they are correct only within 3–5 %. For an accuracy of 1 % and less one must determine T_c more precisely. This can be achieved by use of the T -dependence of the largest eigenvalue $E_0(T)$ of the stability matrix [1], since $(1 - E_0(T))^2 \sim T_c - T$ for $T \leq T_c$.

From this table we recognize that the center of mass modes ($l = m = 0$) freeze at $T_c^{l=0} \cong 0.383$ independent on l_{co} and SDA or WDA. This transition is of type B. Ideal glass transitions for $l = 1$ and 2 occur at lower temperatures. Their transition scenario depends on whether $l_{co} = 1$ or $l_{co} = 2$. In case that $l_{co} = 1$, i.e. all $l \geq 2$ are neglected, a type-A transition of $f_1^m(q)$ exists at 0.192 for WDA and at a slightly lower value of 0.187 for SDA. But for $l_{co} = 2$ both modes with $l = 1$ and $l = 2$ *simultaneously* freeze at $T_c^{l=1} = T_c^{l=2} \cong 0.310(0.256)$ for WDA (SDA). This transition is of type B for $l = 2$ and $l = 1$. Whereas $l = 2$ *must* freeze via a discontinuous (type-B)

transition, $l = 1$ could undergo a continuous transition (type-A). The coupling between the modes with $l = 1$ and $l = 2$ in eq.(17) is obviously large enough to lead to a type-B transition for $l = 1$, too. These possible scenarios are in accordance with the discussion at the end of section II. Since for WDA the r.h.s. of eq.(14) contains more contributions from the coupling between ODOF and TDOF than for SDA, it is reasonable that the critical temperatures for WDA are larger (or equal) than those for SDA.

The NEP $(f_l^m)_c^{MD}$ obtained from the MD-simulation [22] by a fit with the von Schweidler law and $(f_l^m)^{MCT}$ from molecular MCT for $l_{co} = 2$, WDA and $T = T_c^{l=1} = T_c^{l=2} \cong 0.310$ are shown in Figure 2. Whereas $(f_l^m)_c^{MD}$ for $l = 0, 1, 2$ and $(f_l^m)^{MCT}$ for $l = 1, 2$ are the *critical* NEP, this is not true for $(f_0^0)^{MCT}$, since $T_c^{l=0} > 0.310$. Despite the approximations we made, the q -dependence of $(f_l^m)_c^{MD}$ is reasonably well reproduced by the MCT-result. Even the shoulder in $(f_0^0)_c^{MD}$ at $q \approx 3$ is reproduced as a small hump at that q -value. Apart from this prepeak, the q -variation of f_l^m is in phase with that of the corresponding static correlators (cf. Fig.1). Whereas $(f_0^0)^{MCT} > (f_0^0)_c^{MD}$ (as expected again, due to the mean field character of MCT) the opposite is true for f_l^m with $l = 1$ and 2. For SDA the result for $(f_l^m)^{MCT}$ at $T = T_c^{l=1} = T_c^{l=2} \cong 0.256$ (not shown in Figure 2) is about 5 - 10 % below the corresponding result for WDA.

	$T_c^{l=0}$	$T_c^{l=1}$	$T_c^{l=2}$
$l_{co} = 0$	0.383 (0.383)	—	—
$l_{co} = 1$	0.383 (0.383)	0.192 (0.187)	—
$l_{co} = 2$	0.383 (0.383)	0.310 (0.256)	0.310 (0.256)

TABLE I. Critical temperatures T_c^l for $l_{co} = 0, 1, 2$ and WDA. The corresponding values for SDA are given in parantheses.

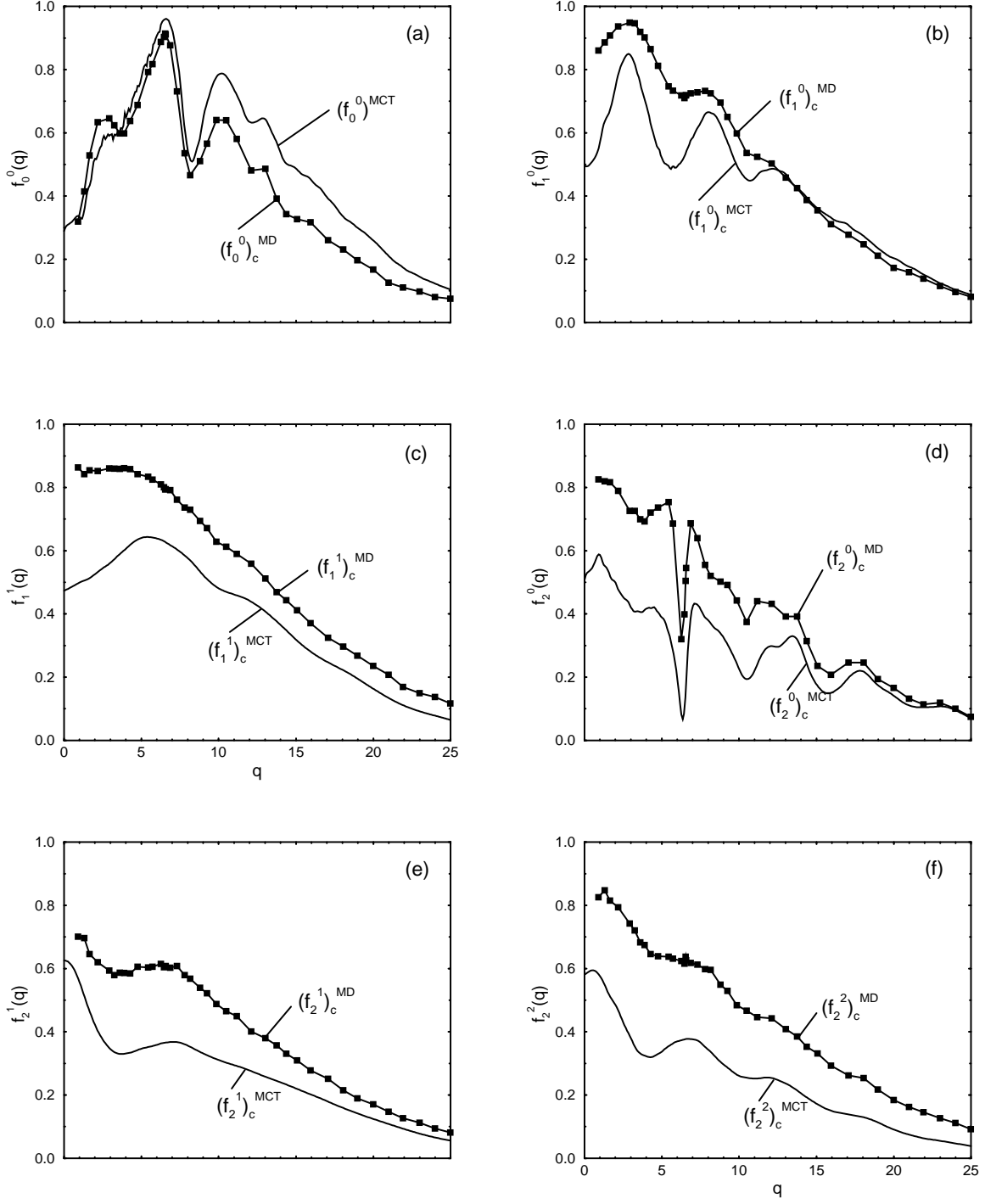


FIG. 2. q -dependence of the critical nonergodicity parameters $(f_l^m)_c^{MD}$ from the MD-simulation and of $(f_l^m)_c^{MCT}$ for $T \cong 0.310$: (a) $l = m = 0$, (b) $l = 1, m = 0$, (c) $l = 1, m = 1$, (d) $l = 2, m = 0$, (e) $l = 2, m = 1$ and (f) $l = 2, m = 2$.

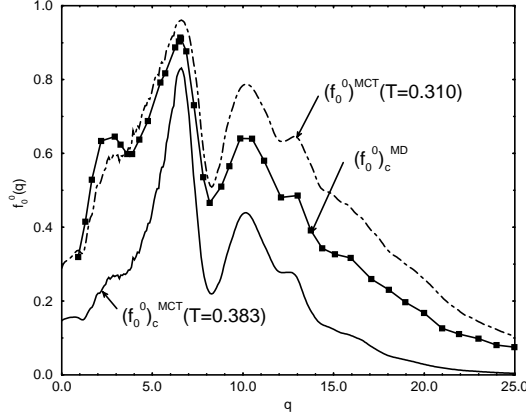


FIG. 3. Comparison of $(f_0^0)^{MD}$, $(f_0^0)^{MCT}(T_c^{l=0} \cong 0.383)$ and $(f_0^0)^{MCT}(T \cong 0.310)$.

Finally we compare $(f_0^0)^{MCT}$ at $T = T_c^{l=0} = 0.383$, i.e. the critical NEP, with that at $T \approx 0.310$. The result, including $(f_0^0)^{MD}$ is given in Figure 3. Now, we also find that $(f_0^0)^{MCT} < (f_0^0)^{MD}$. That $(f_0^0)^{MCT} < (f_0^0)^{MCT}(T \cong 0.310)$ is trivial, because f_l^m increases monotonously with decreasing temperature.

V. SUMMARY AND CONCLUSIONS

For the first time, we have compared numerical results for a molecular liquid of diatomic, rigid molecules [20–22] with the corresponding results from *molecular* MCT for linear molecules, which was worked out recently [15,18]. This comparison was done for the nonergodicity parameters $f_l^m(q)$. First of all, we find that MCT does not yield an ideal glass transition in the temperature range of the simulation. This is quite similar to what has been found for the MD-simulation of water [12,13], but is in variance with the behavior for simple Lennard–Jones liquids [7,8] and hard spheres [1,2]. For the hard sphere system this means that the critical density n_c from MCT is *less* than the experimental value. This difference between simple and molecular liquids probably reveals the role of ODOF and their coupling to TDOF. This coupling is underestimated by both diagonalization approximations we used. With these approximations the ideal glass transition occurs below T_c^{MD} , only. The existence of two different transition temperatures for $l_{co} = 1$ and $l_{co} = 2$ we believe is an artifact of the diagonalization approximation (with respect to l). Nevertheless, the q -dependence of $(f_l^m)^{MD}$ is reasonably well reproduced by the corresponding MCT-result. Whether the hump in $(f_0^0)^{MCT}$ at $q \approx 3$, which relates to the shoulder of $(f_0^0)^{MD}$ at the same q -value is genuine can not presently be decided. But it is interesting that a similar hump in the critical NEP has recently been found for the *molecular*

glass former orthoterphenyl [23]. Whether its existence in the nonergodicity parameter $(f_0^0(q))_c$ for the center of mass motion is an indirect influence of the ODOF or not remains an open question. For OTP this prepeak may be related to an *intramolecular* property, not related to ODOF [24].

To obtain the MCT-results presented in this paper already a considerable numerical effort was necessary. Nevertheless it will be important to solve the MCT-equations without any diagonalization approximation, which we believe guarantees (for our molecules) the existence of a *single* transition temperature T_c^{MCT} . In this respect we also would like to mention that, e.g. the *nondiagonal*, static correlator $S_{20}^0(q)$ is of the same order as $S_{00}^0(q)$ [22], i.e. it should not be neglected. Without assuming diagonality with respect to l , more contributions to the translational-rotational coupling will be taken into account which we expect to yield a higher value for T_c^{MCT} . If in that case and for $l_{co} = 2$ it would be still $T_c^{MCT} < T_c^{MD}$, this would indicate that also correlators with $l > 2$ have to be taken into account, as it was done for the single dumbbell in an isotropic liquid of hard spheres, however, using SDA [14]. In ref. [14] it has been found that a one percent accuracy of $(f_l^m)_c$ requires to take into account correlators up to $l + 2$. But on the other hand our investigation shows that the SDA may introduce an error of 5–10 %. Therefore, in order to get reliable results for the NEP, e.g. $(f_2^m)_c$ one has to remove both the diagonalization approximation and the restriction to $l \leq 2$.

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